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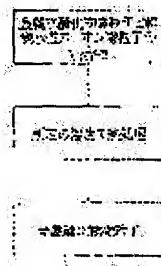
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## (54) METHOD FOR PRODUCING METAL OXIDE PARTICULATE POWDER

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a new technology for producing a metal oxide particulate powder, which allows the production of a large amount of metal oxide particulate powder containing primary particles each having a small diameter of  $\leq 10$  nm, which powder has been difficult to be produced in a large amount by a conventional method.

SOLUTION: The method for producing the metal oxide particulate powder comprises heat treating a mixture, obtained by mixing a gel-like precipitate containing a prescribed metal ion with carbon or carbon-like fine particulate powder, at a predetermined temperature in a nonreducing atmosphere. The carbon or carbon-like fine particulate powder is super-hydrophilic. A mass-production technology of metal oxide particulate powder, which allows the mass-production of nanoparticles of various metal oxides having primary particle diameters of  $\leq 10$  nm, is provided.



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**CLAIMS**

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[Claim(s)]

[Claim 1]

It is the method of manufacturing metal oxide particle powder by heat-treating a mixture which a gel sediment, carbon, or carbon Mr. particle powder containing a predetermined metal ion mixed with prescribed temperature in nonreduction atmosphere, A manufacturing method of metal oxide particle powder, wherein said carbon or carbon Mr. particle powder is super-hydrophilic nature.

[Claim 2]

A mixing process with which a mixture which a gel sediment, super-hydrophilic carbon, or carbon Mr. particle powder containing said predetermined metal ion mixed mixes said super-hydrophilic carbon or carbon Mr. particle powder to an acidic solution containing a predetermined metal ion, A precipitation process which deposits a gel sediment of predetermined metal by adding an alkaline aqueous solution to an acidic solution which the super-hydrophilic carbon or carbon Mr. particle powder mixed, A manufacturing method of a recovery process which collects mixtures of the gel sediment and super-hydrophilic carbon, or carbon Mr. particle powder from a solution in which the gel sediment deposited, and the metal oxide particle powder according to claim 1 which is what is alike and is manufactured more.

[Claim 3]

A mixture which a gel sediment, super-hydrophilic carbon, or carbon Mr. particle powder containing said predetermined metal ion mixed, A precipitation process which deposits a gel sediment which contains a predetermined metal ion by adding an alkaline aqueous solution to an acidic solution containing a predetermined metal ion, A recovery process which collects gel sediments containing the metal ion from a solution in which a gel sediment containing the metal ion deposited, A manufacturing method of the metal oxide particle powder according to claim 1 which resembles a gel sediment containing the collected metal ion with a mixing process which mixes super-hydrophilic carbon or carbon Mr. particle powder, and is manufactured more.

[Claim 4]

A manufacturing method of the metal oxide particle powder according to claim 1 in which said

super-hydrophilic nature carbon particulates are super-hydrophilic nature carbon black particulates.

[Claim 5]

A manufacturing method of the metal oxide particle powder according to claim 1 whose underwater diameter of floc of said super-hydrophilic nature carbon-particulates powder is about 200 nm or less.

[Claim 6]

A manufacturing method of the metal oxide particle powder according to claim 1 in which a functional group of hydrophilic nature exists in the particle surface of said super-hydrophilic nature carbon-particulates powder.

[Claim 7]

A manufacturing method of the metal oxide particle powder according to claim 6 whose functional group of hydrophilic nature in the particle surface of said super-hydrophilic nature carbon-particulates powder is a carboxyl group.

[Claim 8]

A manufacturing method of metal oxide particle powder given in any 1 paragraph of claims 1-3 which are what said super-hydrophilic carbon Mr. particle powder is an organic compound of super-hydrophilic nature, and gasifies by oxidation.

[Claim 9]

A manufacturing method of the metal oxide particle powder according to claim 1 in which said predetermined metal is silicon, manganese, a zirconium, chromium, iron, nickel, tin, zinc, indium, aluminum, cerium, magnesium, and one or more sorts of metal chosen from among titanium.

[Claim 10]

A manufacturing method of the metal oxide particle powder according to claim 2 or 3 which produces said acidic solution by dissolving a salt of said predetermined metal in a solvent.

[Claim 11]

A manufacturing method of the metal oxide particle powder according to claim 10 whose salts of said metal are either a nitrate, carbonate, sulfate, acetate and a chloride.

[Claim 12]

A manufacturing method of the metal oxide particle powder according to claim 2 or 3 in which said alkaline aqueous solution is an ammonia solution.

[Claim 13]

A manufacturing method of the metal oxide particle powder according to claim 1 in which said heat treatment is performed by heating with a maximum temperature within the limits of 400-1000 \*\*.

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[Translation done.]



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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[Field of the Invention]

[0001]

This invention relates to the method of manufacturing the metal oxide particle powder provided with nano-scale detailed particle diameter.

It is a thing about the new production technology of the metal oxide particle powder which has the particle diameter of the nano size which makes it possible to manufacture the nano particle of various metallic oxides which has the fine primary particle diameter of 10 nm or less detailed, for example when material of 50 nm or less is generally the tin oxide in large quantities, In heat treatment of the heat treatment process at the time of metal oxide particle manufacture, and the metal oxide particle after manufacture, it is related with the new art providing the powder which cannot carry out grain growth easily.

[0002]

In the field of electronic ceramics for example, this invention, While it is requested strongly that the nano particle which has the primary particle diameter of nano size as raw material ceramics should be produced in large quantities, in a conventional method. It is developed based on it having been difficult to produce a nano particle of 30 nm or less in large quantities, In a conventional method, the new mass production art of a nano particle in which producing makes it possible to produce the nano particle of a metallic oxide which has the difficult primary particle diameter of 10 nm or less in large quantities is provided. this invention has a high technical meaning as the mass production art which can put in practical use the nano particle of various metallic oxides which has the fine primary particle diameter of 10 nm or less, and new nano particle manufacturing technique for which the existing production technology of a nano particle can be substituted.

[Background of the Invention]

[0003]

It is possible to obtain a metallic oxide by adding an alkaline aqueous solution to the acidic solution containing a metal ion, producing a gel sediment, collecting these and adding heat

treatment to this. This kind of method is generally called the sedimentation method. In this method, a primary particle turns into a firmly united coarse particle (aggregated particle) on a drying stage story. Therefore, even if it ground this mechanically, while secondary particle diameter was not less than several about micrometers, it was a problem that an impurity mixes at the time of grinding.

[0004]

The method of manufacturing the metal oxide particle powder which improved the above-mentioned sedimentation method to a prior art reference that this should be solved is indicated. For example, carbon is added to the acidic solution which is the stage before producing (1) sediment, an alkaline aqueous solution is added to it, a sediment is generated, and the manufacturing method of the metal oxide particle powder which consists of calcinating it is proposed (patent documents 1). By this kind of method, it is reported that primary particle diameter is 30 nm to 50 nm.

[0005]

(2) -- the method of oxidizing the graphite lamellar compound which metallic compounds and graphite denaturation things, such as a nitrate and a oxynitrate, were made to react, and was generated as a method of it being detailed and obtaining the metal oxide powder of a high grade is proposed (patent documents 2). However, in this kind of method, since a long time is needed for that metal is restricted to what can form a graphite lamellar compound, and formation of that graphite lamellar compound, manufacturing methods of a nano particle include the problem of not being suitable for mass production.

[0006]

As a method of manufacturing the metal oxide particle powder which improved (3) sedimentation methods, after a sediment generates, solution, the separated sediment, and carbon are added by filtration, and the manufacturing method of the metal oxide particle powder which calcinates it is proposed (patent documents 3). In this method, it is indicated that particle diameter is about 50 nm. Although the method indicated by these prior art references is a simple method, particle diameter is not less than about 30 nm.

It was difficult to obtain still finer primary particle diameter in this kind of method.

[0007]

Thus, although it had the feature of the powder obtained being excellent in dispersibility, and the method being simple, and being a process which can be mass-produced, in the improved sedimentation method which was indicated with the above-mentioned prior art reference, there was a problem that it was difficult to obtain still finer primary particle diameter.

[0008]

[Patent documents 1] JP,61-122121,A

[Patent documents 2] JP,7-187668,A

[Patent documents 3] JP,2002-255515,A

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0009]

The result of having repeated research wholeheartedly in such a situation for the purpose of developing the new mass production art of the nano particle which enables this invention persons to obtain still finer primary particle diameter in view of the above-mentioned conventional technology, By adopting the sedimentation method which adds carbon-particulates powder to a gel sediment, or the sedimentation method which adds carbon-particulates powder to a solution beforehand, and obtains the sediment on gel, it succeeds in manufacturing the auric acid ghost particle powder which has still finer primary particle diameter, and came to complete this invention. An object of this invention is to provide the new production technology of the metallic-oxide nano particle which makes it possible to manufacture the metal oxide particle powder provided with nano-scale detailed particle diameter in large quantities.

[Means for Solving the Problem]

[0010]

This invention for solving an aforementioned problem comprises the following technical means.

(1) It is the method of manufacturing metal oxide particle powder by heat-treating a mixture which a gel sediment, carbon, or carbon Mr. particle powder containing a predetermined metal ion mixed with prescribed temperature in nonreduction atmosphere, A manufacturing method of metal oxide particle powder, wherein said carbon or carbon Mr. particle powder is super-hydrophilic nature.

(2) A mixture which a gel sediment, super-hydrophilic carbon, or carbon Mr. particle powder containing said predetermined metal ion mixed, A mixing process which mixes said super-hydrophilic carbon or carbon Mr. particle powder to an acidic solution containing a predetermined metal ion, A precipitation process which deposits a gel sediment of predetermined metal by adding an alkaline aqueous solution to an acidic solution which the super-hydrophilic carbon or carbon Mr. particle powder mixed, A manufacturing method of metal oxide particle powder given in a recovery process which collects mixtures of the gel sediment and super-hydrophilic carbon, or carbon Mr. particle powder from a solution in which the gel sediment deposited, and the above (1) which is what is alike and is manufactured more.

(3) A mixture which a gel sediment, super-hydrophilic carbon, or carbon Mr. particle powder containing said predetermined metal ion mixed, A precipitation process which deposits a gel sediment which contains a predetermined metal ion by adding an alkaline aqueous solution to an acidic solution containing a predetermined metal ion, A recovery process which collects gel sediments containing the metal ion from a solution in which a gel sediment containing the metal ion deposited, A manufacturing method of metal oxide particle powder given in the above (1) which resembles a gel sediment containing the collected metal ion with a mixing process which mixes super-hydrophilic carbon or carbon Mr. particle powder, and is manufactured more.

(4) A manufacturing method of metal oxide particle powder given in the above (1) in which said

super-hydrophilic nature carbon particulates are super-hydrophilic nature carbon black particulates.

(5) A manufacturing method of metal oxide particle powder given in the above (1) whose underwater diameter of floc of said super-hydrophilic nature carbon-particulates powder is about 200 nm or less.

(6) A manufacturing method of metal oxide particle powder given in the above (1) in which a functional group of hydrophilic nature exists in the particle surface of said super-hydrophilic nature carbon-particulates powder.

(7) A manufacturing method of metal oxide particle powder given in the above (6) whose functional group of hydrophilic nature in the particle surface of said super-hydrophilic nature carbon-particulates powder is a carboxyl group.

(8) A manufacturing method of metal oxide particle powder given in any 1 paragraph of the above (1) which is what said super-hydrophilic carbon Mr. particle powder is an organic compound of super-hydrophilic nature, and gasifies by oxidation to (3).

(9) A manufacturing method of metal oxide particle powder given in the above (1) in which said predetermined metal is silicon, manganese, a zirconium, chromium, iron, nickel, tin, zinc, indium, aluminum, cerium, magnesium, and one or more sorts of metal chosen from among titanium.

(10) A manufacturing method of the above (2) which produces said acidic solution by dissolving a salt of said predetermined metal in a solvent, or metal oxide particle powder given in (3).

(11) A manufacturing method of metal oxide particle powder given in the above (10) whose salts of said metal are either a nitrate, carbonate, sulfate, acetate and a chloride.

(12) A manufacturing method of the above (2) in which said alkaline aqueous solution is an ammonia solution, or metal oxide particle powder given in (3).

(13) A manufacturing method of metal oxide particle powder given in the above (1) performed when said heat treatment heats with a maximum temperature within the limits of 400-1000 \*\*. [0011]

Next, it explains still in detail about this invention.

This invention is the method of manufacturing metal oxide particle powder by heat-treating a mixture which a gel sediment, carbon, or carbon Mr. particle powder containing a predetermined metal ion mixed with prescribed temperature in nonreduction atmosphere, It is characterized by said carbon or carbon Mr. particle powder being super-hydrophilic nature. In this invention, metal oxide particle powder is defined as what means a metal oxide particle and/or its powder.

[0012]

A flow chart until it heat-treats a mixture which a gel sediment containing a predetermined metal ion and super-hydrophilic nature carbon particulates mixed at a predetermined temperature and obtains metal oxide particle powder is shown in drawing 1. Here, carbon-particulates powder mixed with a gel sediment is the feature of the maximum [ be / it / super-hydrophilic nature carbon-particulates powder ] of this invention.



[0013]

This super-hydrophilic nature carbon-particulates powder is clearly distinguished from carbon of the usual hydrophilic nature. It is used in a meaning that usual hydrophilic carbon is not hydrophobicity, and when it adds in water, all are called hydrophilic nature if it is easy to adapt itself to water.

[0014]

Super-hydrophilic nature in this invention needs to have very good dispersibility in inside of distilled water, and a diameter of average floc of carbon in inside of distilled water (second [ an average of ] particle diameter) means being about 1 micrometer and being about 200 nm or less more preferably from 10 nm. A diameter of average floc of carbon in inside of distilled water can be measured by dynamic light scattering etc., for example. As carbon, carbon black is used preferably. Super-hydrophilic nature carbon particulates have a functional group of hydrophilic nature preferably, and the functional group is a carboxyl group still more preferably.

[0015]

Instead of said super-hydrophilic nature carbon particulates, it is an organic compound of super-hydrophilic nature as carbon Mr. particles, and even if it uses what is gasified by oxidation, same effect is expected. Carbon Mr. particle powder is an organic compound of super-hydrophilic nature [ above ], and this invention is defined as what means what is gasified by oxidation. A method of preparing a mixture which a gel sediment containing a predetermined metal ion and super-hydrophilic nature carbon particulates mixed is mentioned later.

[0016]

In this invention, one sort or two or more metal ions which were chosen from among silicon, manganese, a zirconium, chromium, iron, nickel, tin, zinc, indium, aluminum, cerium, magnesium, and titanium are illustrated as a predetermined metal ion.

[0017]

In this invention, a mixture which a gel sediment containing a predetermined metal ion and carbon-particulates powder mixed is prepared, next it progresses to a process of heat treatment at a predetermined temperature. Here, by heat treatment, carbon reacts to oxygen in atmosphere, and it becomes carbon dioxide, and is removed.

[0018]

In this process, it dries to such an extent that moisture which remained into a mixture which a gel sediment containing a predetermined metal ion and carbon-particulates powder usually mixed is fully removed, and baking treatment is further performed at temperature which an oxide generates in nonreduction atmosphere. It is preferred to set drying temperature as 200 °C from 50 °C, and to set calcination temperature as about 1000 °C from 400 °C, for example. If heat treatment with the above prescribed temperature is finished, metal oxide particle powder whose primary particle diameter is 10 nm or less will be obtained.

[0019]

Next, a manufacturing method of a mixture which a gel sediment and super-hydrophilic nature

carbon-particulates powder containing a predetermined metal ion mixed is explained. Two methods are mentioned as a method of producing a mixture which a gel sediment and super-hydrophilic nature carbon-particulates powder containing this predetermined metal ion mixed. One is the manufacturing method A (drawing 2), and another is the manufacturing method B (drawing 3).

[0020]

First, the manufacturing method A is explained. If an acidic solution containing predetermined metal, i.e., a metal ion which constitutes a metallic oxide which it is going to manufacture, can be produced, the method in particular will not be limited for a manufacturing method of an acidic solution containing a predetermined metal ion. For example, it can be dissolved in distilled water by this acidic solution, and it can produce a nitrate, carbonate, sulfate, acetate, or a chloride containing a predetermined metal ion. Water-soluble alcohol etc. may be sufficient as a solvent besides water.

[0021]

Next, said carbon-particulates powder of super-hydrophilic nature is added to this acidic solution. After adding super-hydrophilic nature carbon-particulates powder, it fully stirs. At this time, it is good to stir and to stir using a stirrer or an ultrasonic homogenizer so that carbon particulates may fully be distributed. An alkaline aqueous solution is added to an acidic solution which added super-hydrophilic nature carbon particulates after stirring. Ammonia solution of an alkaline aqueous solution etc. are preferred. When an alkaline aqueous solution is added, a gel sediment in which super-hydrophilic nature carbon particulates were distributed deposits. This gel sediment is predetermined metal hydroxide, a metal hydrated oxide, or a metallic-oxide hydrate.

[0022]

Next, gel sediments in which the super-hydrophilic nature carbon particulates were distributed are collected from a solution in which a gel sediment in which super-hydrophilic nature carbon particulates were distributed deposited. In this process, if it is the way a gel sediment in which carbon particulates were distributed is selectively recoverable from a solution, a proper method will be used. For example, a method by a filtration process and a washing process of solution is simple. A centrifuge method etc. are possible. In this way, a mixture which a gel sediment containing a predetermined metal ion and super-hydrophilic nature carbon particulates mixed is obtained.

[0023]

Next, the manufacturing method B is explained based on drawing 3. An alkaline aqueous solution is added to an acidic solution containing a predetermined metal ion produced in the manufacturing method A and a similar way. This alkaline aqueous solution may be the same as that of the manufacturing method A. When an alkaline aqueous solution is added, metal hydroxide or metal hydrated oxide particles deposit as a gel sediment.

[0024]

The gel sediments are collected from a solution in which a gel sediment deposited. This recovery method may be the same as the manufacturing method A. Super-hydrophilic nature

carbon-particulates powder is added to a gel sediment containing a collected predetermined metal ion, and it mixes. A mixing method in particular is not limited. For example, it mixes using a roll mill, a planet type mixer, etc. Thus, a gel sediment and a mixture of super-hydrophilic nature carbon particulates containing a predetermined metal ion are obtained.

[0025]

In a strongly acidic solution, when dispersibility is bad, the manufacturing method B of super-hydrophilic nature carbon-particulates powder is more preferred. A partner to whom this adds super-hydrophilic nature carbon-particulates powder in the manufacturing method B is a sediment, and, as for a sediment, generally shows alkalinity from neutrality. From this, the dispersibility of super-hydrophilic nature carbon particulates is not worsened. On the other hand, in the manufacturing method A, super-hydrophilic nature carbon-particulates powder is added into an acidic solution. For this reason, if an acidic solution is the acescence, it will be satisfactory, but when strong acid nature is shown, the dispersibility of super-hydrophilic nature carbon-particulates powder worsens, and particle powder of thin primary particle diameter can be obtained as a result.

[0026]

Although obtaining a metal oxide particle by heat-treating a mixture obtained by mixing carbon particulates to sediments, such as collected metal hydroxide, with a sedimentation method with prescribed temperature was performed in a conventional method, metal oxide particle powder provided with detailed particle diameter, It was difficult for fine primary particle diameter to produce a nano particle of 30 nm or less in large quantities. On the other hand, by using super-hydrophilic nature carbon particulates in a method of this invention, It is possible to mass-produce a nano particle of a metallic oxide which has the nothing fine primary particle diameter of cut profitable 10 nm or less in a conventional method, and this invention is useful as industrial nano particle manufacturing technique which enables fertilization of a nano particle. Metal oxide particle powder manufactured by this invention has the feature of being hard to carry out grain growth, also by subsequent heat treatment.

[Effect of the Invention]

[0027]

(2) [ from which the metal oxide particle powder which has the fine primary particle diameter of (1) of 10 nm or less is obtained by this invention ] the powder obtained, (3) which does not need to be mechanically ground since it excels in dispersibility, in order not to grind mechanically, The method of (4) (5) which can provide process which can be mass-produced [ that it is simple and ] by low cost this invention without mixing of an impurity, The effect of being hard to carry out grain growth of the particle powder obtained by the method of (6) this inventions suitably applicable as mass production technology of the nano particle of various metallic oxides by a subsequent heat treatment process is done so.

[Best Mode of Carrying Out the Invention]

[0028]

Next, although an example explains this invention still more concretely, this invention is not limited at all by the following examples.

[Example 1]

[0029]

Tin-oxide particle powder was manufactured in this example, using tin ion as a predetermined metal ion. As a method of producing the mixture which the gel sediment containing tin ion and super-hydrophilic nature carbon black fine particle powder mixed, the manufacturing method B shown in drawing 3 was used. 500 cm of distilled water<sup>3</sup> was added to the tin tetrachloride 5 hydrate 17.5g, and tin tetrachloride solution was produced by fully stirring. In this case, the concentration of the tin tetrachloride was 0.10 mol/dm<sup>3</sup>. In this solution, the tin tetrachloride is ionized at tin ion Sn<sup>4+</sup> and chloride ion Cl<sup>-</sup>. The process of producing this tin tetrachloride solution corresponds to an acidic solution making process.

[0030]

Next, it is 20-cm<sup>3</sup> \*\*\*\*\* about 25% of ammonia solution to this, stirring this solution. Thereby, the reaction arose and gel white precipitate generated. This white sediment is tin hydroxide or a tin hydrated oxide. This corresponds to the process of obtaining the gel sediment containing a metal ion.

[0031]

Next, filtration recovered the white sediment from solution. However, washing of a sediment and filtration for the second time were performed 3 times from 2 in order to remove impurities, such as ammonium ion and chloride ion, from a sediment. This corresponds to a filtration process.

[0032]

Next, the super-hydrophilic nature carbon black fine particle powder 1.26g was added to the collected white sediment 7g, and it mixed by the planet type mixer. This corresponds to a mixing process. That is, the mixture which the gel sediment containing tin ion and super-hydrophilic nature carbon black fine particle powder mixed at this process was obtained. Here, the diameter of average floc in the inside of the distilled water of the super-hydrophilic nature carbon black fine particle powder used by this example was 100 nm.

[0033]

Next, this mixture was dried from 10 hours at 70 \*\* for about 20 hours. Thereby, the moisture contained in an inside was fully removed. What is obtained by this is called a dried body. Next, the above-mentioned dried body was heat-treated on conditions (600 \*\* and 4 h) among the atmosphere using the muffle furnace. Thereby, tin-oxide particle powder was obtained.

[0034]

Comparative examples 1 and 2

As the comparative examples 1 and 2, the same examination was done by the same method as Example 1, using respectively the carbon black fine particle powder (carbon black fine particle powder A and B) which is not super-hydrophilic nature as a substitute of super-hydrophilic nature carbon black fine particle powder.

[0035]

About the carbon black fine particle powder used for Example 1 and the comparative examples

1 and 2, when X diffraction (XRD) analysis was conducted, the difference was not looked at by three kinds of XRD patterns. When three kinds of carbon black fine particle powder were added to distilled water at 20wt% of a rate and was observed visually, super-hydrophilic nature carbon black fine particle powder had good dispersibility. On the other hand, the carbon black fine particle powder A and B had bad dispersibility, and precipitated immediately.

[0036]

When the particle diameter in the inside of distilled water was investigated with the dynamic-light-scattering particle-size-distribution plan, super-hydrophilic nature carbon black fine particle powder was 100 nm in mean particle diameter, and the carbon black fine particle powder A and B was not less than 10 micrometers. That is, in distilled water, super-hydrophilic nature carbon black fine particle powder had [ distribution of the above-mentioned particle diameter ] good dispersibility, and, on the other hand, it was shown that the carbon black fine particle powder A and B has bad dispersibility. This result was in agreement with the result of above-mentioned viewing.

[0037]

The infrared absorption pattern of the carbon black fine particle powder used for Example 1 and the comparative examples 1 and 2 is shown in drawing 4. The absorption peak was observed near  $1600\text{ cm}^{-1}$  and near  $3400\text{ cm}^{-1}$  by super-hydrophilic nature carbon black. Although the absorption resulting from C=O and the absorption resulting from C=N existed near  $1600\text{ cm}^{-1}$ , it was checked by ultimate analysis that N is hardly contained in super-hydrophilic nature carbon black.

[0038]

Therefore, it was concluded that the peak near  $1600\text{ cm}^{-1}$  originated in C=O. The peak considered that near  $3400\text{ cm}^{-1}$  originates in O-H existed. From the above thing, it was concluded that the carboxyl group of hydrophilic nature existed in the surface of super-hydrophilic nature carbon black.

[0039]

The XRD pattern of the tin-oxide particle powder obtained by Example 1 and the comparative examples 1 and 2 is shown in drawing 5. The tin-oxide particle powder of Example 1 had the half breadth of the diffraction peak wider than the tin-oxide particle powder of the comparative examples 1 and 2. When 2 theta measured in detail the peak which are 26.7 degrees, 33.4 degrees, 51.9 degrees, and 78.8 degrees and it asked for the size of microcrystal from the formula of Hall, it became as it is shown in Table 1, and the tin-oxide particle powder of Example 1 found that microcrystal was smaller than the tin-oxide particle powder of the comparative examples 1 and 2.

[0040]

[Table 1]

## 酸化スズ微粒子粉末の結晶子サイズ

酸化スズ微粒子粉末	結晶子の大きさ(nm)	歪 (%)
実施例 1	7.5±1.0	0.2
比較例 1	18.9±1.0	0.1
比較例 2	18.3±1.6	0.1

[0041]

The transmission electron microscope photograph of Example 1, the comparative example 1, and the comparative example 2 is shown in drawing 6, and 7 and 8, respectively. The particle diameter of the tin oxide of Example 1 was clearly smaller than the tin oxide of the comparative examples 1 and 2. In Example 1, it was mostly in agreement with the particle diameter observed with the transmission electron microscope, and the crystallite size in Table 1. It was proved that the particle powder in which primary particle diameter has the particle diameter below half at 10 nm or less by using carbon black of super-hydrophilic nature compared with the thing not using this simple was obtained from the above thing.

[Example 2]

[0042]

In this example, the dried body of the mixture which the gel sediment containing tin ion and super-hydrophilic nature carbon black fine particle powder mixed by the same method as Example 1 was obtained.

[0043]

Comparative example 3

The dried body of the mixture which the gel sediment and super-hydrophilic nature carbon-particulates powder black containing tin ion mixed by the same method as the comparative example 1 was obtained.

[0044]

The transmission electron microscope photograph of Example 2 and the comparative example 3 is shown in drawing 9 and 10, respectively. An about 20-nm light gray particle is visible to drawing 9 and 10. This is a primary particle of carbon black. In drawing 9, the surface of this carbon black was dispersedly dotted with the very small blackish particles of the color compared with drawing 10. The very small blackish particles of this color are the hydrated oxides of tin.

H<sub>2</sub>O is included.

On the other hand, in drawing 10, the very small blackish particles of the color existed in the specific place of the primary particle surface of carbon black intensively. If these differences are considered, it can be said that the cause of super-hydrophilic nature is because the functional group of the hydrophilic nature which exists in the carbon surface exists.

[0045]

Since the functional group of this hydrophilic nature existed, the hydrated oxide of tin containing  $H_2O$  has distributed and existed in the carbon surface, but since the functional group of hydrophilic nature does not exist in usual carbon, it is thought that the hydrated oxide of tin will not be condensed and that the difference in such an organization arose. Although the difference in such fine texture of a dried body is considered to have been reflected in the difference in the primary particle diameter of the tin oxide after calcination, this is considered below.

[0046]

In the case of super-hydrophilic nature carbon black of Example 2, the hydrated oxide of tin distributed and existed on the surface of carbon black. For this reason, although grain growth arises during calcination, since the grade of condensation is small, the grade of grain growth is considered that were small and the tin oxide with a primary particle diameter of 10 nm or less was obtained. On the other hand, in the case of the carbon black A of the comparative example 3, the hydrated oxide of tin was condensing comparatively greatly on the surface of carbon black. For this reason, it is easy to produce grain growth during calcination, and it is thought that the tin oxide of the primary particle diameter whose primary particle diameter is about 20 nm was obtained.

[Example 3]

[0047]

Cerium oxide particle powder was manufactured in this example, using cerium ion as a predetermined metal ion. As a method of producing the mixture which the gel sediment containing oxidation cerium ion and super-hydrophilic nature carbon black fine particle powder mixed, the manufacturing method B shown in drawing 3 was used. 200 cm of distilled water<sup>3</sup> was added to the cerium nitrate 6 hydrate 8.68g, and cerium nitrate solution was produced by fully stirring. In this case, the concentration of the cerium nitrate was  $0.10 \text{ mol/dm}^3$ . In this solution, the cerium nitrate is ionized at cerium ion  $Ce^{4+}$  and nitrate ion  $NO_3^-$ . The process of producing this cerium nitrate corresponds to an acidic solution making process.

[0048]

Next, it is 10-cm<sup>3</sup> \*\*\*\*\* about 25% of ammonia solution to this, stirring this solution. Thereby, the reaction arose and gel white precipitate generated. This white sediment is hydroxylation cerium or a cerium oxide hydrate. This corresponds to the process of obtaining the gel sediment containing a metal ion. Next, filtration recovered the white sediment from solution. This corresponds to a filtration process.

[0049]

Next, the super-hydrophilic nature carbon black fine particle powder 4.6g was added to the collected white sediment 32g, and it mixed by the planet type mixer. This corresponds to a mixing process. That is, the mixture which the gel sediment containing cerium ion and super-hydrophilic nature carbon black fine particle powder mixed at this process was obtained. Here, the super-hydrophilic nature carbon black fine particle powder used by this example 3 was the

same as what was used in Example 1.

[0050]

Next, this mixture was dried from 10 hours at 70 \*\* for about 20 hours. Thereby, the moisture contained in an inside was fully removed. What is obtained by this is called a dried body. Next, the dried body was divided into the half, and using a muffle furnace, halves are 800 \*\* the conditions of 4 hours in the atmosphere, and halves are 900 \*\* the conditions of 4 hours in the atmosphere, and have already heat-treated the above-mentioned dried body. Thereby, cerium oxide particle powder was obtained.

[0051]

Comparative example 4

As the comparative example 4, the same examination was done by the same method as Example 3, using the carbon black fine particle powder (carbon-black-fine-particle-powder B) which is not super-hydrophilic nature as a substitute of super-hydrophilic nature carbon black fine particle powder. When the X diffraction experiment was conducted on the powder produced by the above-mentioned Example 3 and the comparative example 4 and it asked for crystallite size from the full width at half maximum of the X diffraction pattern using the formula of Hall, it became as it is shown in Table 2.

[0052]

[Table 2]

焼成温度 (°C)	結晶子サイズ (nm)	
	実施例 3	比較例 4
8 0 0	2 2 . 3	3 0 . 0
9 0 0	3 7 . 0	4 1 . 4

[0053]

When calcination temperature was the same, there is a significant difference by the case where super-hydrophilic nature carbon black fine particle powder is used, and the case where that is not right, and the way of the microcrystal in the case of being the former became clear [ a small thing ]. It became clear from this, if super-hydrophilic nature carbon black particulates are used even when compounding cerium oxide particles that the fine thing of microcrystal is obtained, and it was guessed that the art of this invention was applicable also to various materials.

[Example 4]

[0054]

The dried body was produced by the same method as Example 3, it was calcinated after that in 4 hours in the 600 \*\* air, and cerium oxide particle powder was obtained. The powder was further calcinated at 800 \*\*, and the cerium oxide particle powder which added heat treatment was obtained.

[0055]

Comparative example 5



As the comparative example 5, the same examination was done by the same method as Example 4, using the carbon black fine particle powder (carbon-black-fine-particle-powder B) which is not super-hydrophilic nature as a substitute of super-hydrophilic nature carbon black fine particle powder. When the X diffraction experiment was conducted on the powder produced by the above-mentioned Example 4 and the comparative example 5 and it asked for crystallite size from the full width at half maximum of the X diffraction pattern using the formula of Hall, it became as it is shown in Table 3.

[0056]

[Table 3]

800℃の熱処理	結晶子サイズ (nm)	
	実施例 4	比較例 5
前	11.3	14.9
後	23.2	29.0

[0057]

As mentioned above, when super-hydrophilic nature carbon black was used, compared with the case where neither of super-hydrophilic nature carbon black is used an 800 \*\* heat treatment front and after heat treatment, it turned out that crystallite size is small. In Example 4, it of the difference of the crystallite size in heat treatment order was 15.1 nm in the comparative example 5 to 11.9 nm. Therefore, when super-hydrophilic nature carbon black was used, even if it added heat treatment, it became clear that it is hard to carry out grain growth.

[Industrial applicability]

[0058]

As explained in full detail above, this invention relates to the manufacturing method of metal oxide particle powder.

By this invention, the metal oxide particle powder which has the fine primary particle diameter of 10 nm or less can be produced and provided.

Since the metal oxide particle powder obtained by this invention is excellent in dispersibility, it has the advantage that it is not necessary to grind mechanically, therefore there is no mixing of an impurity. The method of this invention is simple, is low cost, and is a process which can be mass-produced.

The primary particle diameter which was difficult to produce in a conventional method is useful as what provides the art from Norio Arata for producing the nano particle with a nano size of 30 nm or less of various metallic oxides in large quantities.

[Brief Description of the Drawings]

[0059]

[Drawing 1]The flow chart from the mixture of metal hydroxide particles and super-hydrophilic

nature carbon particulates which the gel sediment and super-hydrophilic nature carbon-particulates powder containing a predetermined metal ion mixed to a metal oxide particle is shown.

[Drawing 2]The flow chart of the manufacturing method (manufacturing method A) of the mixture of metal hydroxide particles and super-hydrophilic nature carbon particulates which the gel sediment and super-hydrophilic nature carbon-particulates powder containing a predetermined metal ion mixed is shown.

[Drawing 3]The flow chart of the manufacturing method (manufacturing method B) of the mixture of metal hydroxide particles and super-hydrophilic nature carbon particulates which the gel sediment and super-hydrophilic nature carbon-particulates powder containing a predetermined metal ion mixed is shown.

[Drawing 4]The infrared absorption pattern of the various carbon black fine particle powder used for Example 1 and the comparative examples 1 and 2 is shown.

[Drawing 5]The XRD pattern of the various tin-oxide particle powder obtained by Example 1 and the comparative examples 1 and 2 is shown.

[Drawing 6]The transmission electron microscope photograph of the tin oxide powder obtained in Example 1 is shown.

[Drawing 7]The transmission electron microscope photograph of the tin oxide powder obtained by the comparative example 1 is shown.

[Drawing 8]The transmission electron microscope photograph of the tin oxide powder obtained by the comparative example 2 is shown.

[Drawing 9]The transmission electron microscope photograph of the dried body obtained in Example 2 is shown.

[Drawing 10]The transmission electron microscope photograph of the dried body obtained by the comparative example 3 is shown.

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[Translation done.]